

## Claims

[c1] A defect free semipermeable composite membrane comprising:

(i)a support layer which provides mechanical strength and is selected from the group consisting of extruded porous material, non woven material, woven material, braiding material, knitted material, any other rigid or flexible organic or inorganic permeable material,

(ii)a barrier layer which provides selective separation and is selected from the group consisting of at least one hydrophobic polymer as a major component, at least one hydrophilic polymer as a minor component, and polymeric particles as additives,

(iii)a middle layer which covers the rough surface and defects of the support layer, and provides binding between said support and said barrier layers.

[c2] The membrane of claim 1, wherein said middle layer and said outside barrier layer are formed from either the same coating solution or different coating solutions.

[c3] The membrane of claim 1, wherein said middle layer is further selected from the group consisting of epoxy,

polyurethane, silicone, any other adhesive and any other organic or inorganic material which has excellent compatibility between the support and the barrier layers to bond them together.

[c4] The membrane of claim 1, wherein said major component of the barrier layer is a hydrophobic polymer and is selected from the group consisting of poly(vinyl chloride), poly(vinylidene chloride-co-vinyl chloride), poly(vinylidene chloride-co-methyl acrylate), poly(vinylidene chloride-co-acrylonitrile-co-methylmethacrylate), poly(vinylidene chloride-co-acrylonitrile), poly(vinylidene fluoride), poly(vinylidene fluoride-co-hexafluoropropylene), polysulfone, polyethersulfone, polyetherketone, polyacrylonitrile, polystyrene, poly(acrylonitrile-co-butadiene-co-styrene), polyethylene, polypropylene, and combinations thereof.

[c5] The membrane of claim 1, wherein said minor component of the barrier layer is a hydrophilic polymer and is selected from the group consisting of poly(vinyl chloride-co-vinyl acetate-co-vinyl alcohol), poly(vinyl chloride-co-vinyl acetate-co-maleic acid), poly(vinyl acetate-co-vinyl alcohol), poly(vinyl-butyracetal-co-vinylalcohol-co-vinyl acetate), poly(vinyl alcohol-co-ethylene), poly(vinyl alcohol-

co-vinyl acetate-co-itaconic acid), poly(vinyl alcohol), poly(vinyl acetate-co-crotonic acid), poly(1-vinylpyrrolidone-co-vinyl acetate), sulfonated polysulfone, cellulose, cellulose acetate, polyvinylpyrrolidone, poly(vinyl pyridine) and combinations thereof.

[c6] 6he membrane of claim 1, wherein said polymer particles of the barrier layer having particle size from 0.2 nm to 500  $\mu\text{m}$ , and are selected from the group consisting of crosslinked polyvinylpyrrolidone, poly(acrylonitrile-co-methacrylonitrile), crosslinked polystyrene, polyethylene, polypropylene, crosslinked sulfonated polystyrene, crosslinked poly(4-trimethylamino chloride styrene), crosslinked polyethylenimine, crosslinked poly(4-vinylpyridine), poly(4-vinylpyridine) cross-linked, methyl chloride quaternary salt, crosslinked cellulose acetate, anion exchange resin, cation exchange resin, crosslinked sulfonated polysulfone and polyethersulfones, as well as othe crosslinked polymers or combinations thereof.

[c7] 7he membrane of claim 1, wherein said composite membrane is in the form of a hollow fiber.

[c8] 8he membrane of claim 1, wherein said composite membrane is in the form of a tube.

- [c9] The membrane of claim 1, wherein said composite membrane is in the form of a flat sheet.
- [c10] The membrane of claim 1, wherein said composite membrane is in the form of a sphere.
- [c11] The membrane of claim 1, wherein said composite membrane is in the form of any other geometry different from sheet, tube, and sphere.
- [c12] The membrane of claim 1, wherein said membrane has a burst pressure of 10 to 500 psi, a pure water permeability of 1 to 500 gfd/psi, and a rejection of 0 to 100% towards poly(ethylene oxide) molecular weight marker having an average molecular weight of 200,000 daltons.
- [c13] A process for producing a composite membrane comprising:
- (i) preparing a heterogeneous coating solution (dope) containing 8–55% by weight of hydrophobic polymers and 1–50% by weight of hydrophilic polymers, 1–50% by weight of polymer particles as additives, 1–30% by weight of other organic and inorganic additives, and the remaining solvent to make a total percentage of 100,
  - (ii) coating a support with a viscous liquid, which is selected from the group consisting of said dope,

epoxy, polyurethane, silicone, and any other adhesive, to cover the rough surface and defects of said support and to provide a smooth surface and binding for a second coating,

(iii)coating said support again with either the same solution used for the first coating or a different polymer coating solution,

(iv)coagulating said polymer coating layers on top of said support to form a defect free composite membrane in a coagulation bath equipped with an ultrasonic device, which generates ultrasonic vibration to enhance mass transfer and to speed up phase inversion from liquid to solid phase of said coating layers,

(v)removing said solvents and water soluble additives from said coagulated membrane in a leaching bath equipped with an ultrasonic device to enhance mass transfer,

(vi)collecting said composite membrane at a speed of 5 to 600 feet per minute with a take-up wheel immersed in a water bath equipped with an ultrasonic device to remove chemical residuals from said membrane,

(vii)switching to another take-up wheel when one wheel is full to continue collecting said membrane around clock,

(viii)curing said membrane either at ambient temper-

ature or at an elevated temperature depending on the adhesives utilized to bond said support and said membrane together,

(ix) optionally treating said composite membrane with a bleach containing 50 ppm to 120,000 ppm free chlorine at ambient or elevated temperature to increase membrane water permeability by 2 to 10 folds compared to a control membrane never exposed to a chlorine treatment.

[c14] The process according to claim 13, wherein said inorganic additives are selected from the group consisting of copper chloride, lithium chloride, sodium chloride, potassium chloride, calcium chloride, calcium sulfate, calcium carbonate, calcium nitrate, sodium carbonate, sodium bicarbonate, magnesium chloride, aluminum chloride anhydrous, aluminum chloride hexahydrate, ferric chloride, ferrous chloride, sodium hydroxide, calcium sulfate, potassium perchlorate, and combinations thereof.

[c15] The process according to claim 13, wherein said solvent is selected from the group consisting of N,N-dimethylformamide, N,N-dimethyl acetamide, N,N-diethyl acetamide, 2,4-dimethylsulfolane, methyl sulfoxide, 1-methyl-2-pyrrolidinone, trimethyl phosphate, triethyl phosphate, urea, and

1,1,3,3-tetramethylurea, acetone, methyl ethyl ketone, polyethylene glycol alkyl ester, and combinations thereof.

- [c16] The process according to claim 13, wherein said process produces high quality coatings and defect free membranes, which are independent of chemical composition and physical structure of said support, which is selected from the group consisting of flat sheet, hollow fiber, tube, rope, cord, solid wire, a string of hollow and solid spheres, and other continuous materials.
- [c17] 1 spinneret, which has an inlet at the top for a tubular support, an inlet for vacuum suction, and multiple inlets on the side for at least two polymer solutions to coat said tubular support with multiple layers to form a defect free composite hollow fiber membrane.
- [c18] The method of utilizing said composite membranes comprising,
- (i) filtering orange juice containing suspended particles to give a clear filtrate and concentrated orange juice,
  - (ii) filtering lemon juice containing suspended particles to give a clear filtrate and concentrated lemon juice,
  - (iii) filtering any other fruit juice containing sus-

pended particles to give a clear filtered fruit juice and a fruit juice concentrate,

- (iv) filtering vegetable juice,
- (v) filtering red wine containing suspended particles to give a sparkling red wine,
- (vi) filtering white wine containing suspended particles to give a sparkling white wine,
- (vii) filtering milk to give a clear filtrate and a white milk concentrate,
- (viii) filtering soymilk to give a clear and light yellow colored filtrate and a white soymilk concentrate,
- (ix) filtering surface or ground water containing suspended particles to give clear potable water,
- (x) filtering municipal sewage wastewater to give clear dischargeable and resusable water,
- (xi) filtering industrial wastewater to give clear dischargeable and reusable water,
- (xii) filtering bacteria and virus,
- (xiii) filtering air containing airborne particles to give filtered air free of particles,
- (xiv) filtering industrial gases containing airborne particles to give filtered gases free of particles,
- (xv) filtering natural gas containing airborne particles to give filtered natural gas free of particles,
- (xvi) separating small molecules and ions from macromolecules by dialysis.



